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EFFECT OF SILICON SUBSTITUTION ON THE CRYSTAL PROPERTIES OF CYANATE ESTER MONOMERS

17 August 2015

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Outline

- Background / Motivation
  - Cyanate esters
  - Reasons for incorporating silicon into thermosetting resins
- Cyanate esters with Si substituted for C
  - Experimental Studies of Crystalline Properties
  - Heuristic Model Studies of Crystalline Properties
  - Molecular Model Studies of Crystalline Properties

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AFRL Mission

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Cyanate Esters for Next-Generation Aerospace Systems

Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

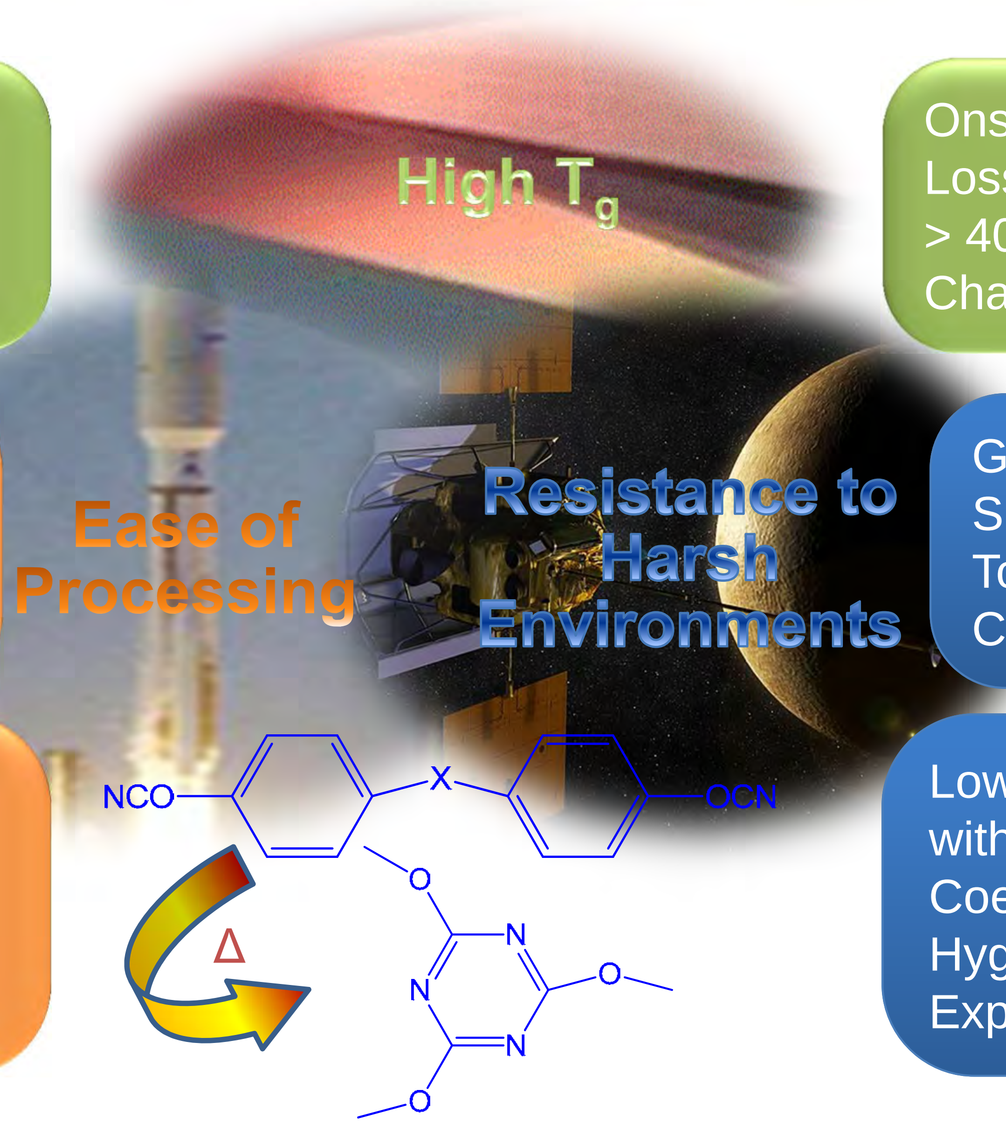
Onset of Weight Loss:
> 400 °C with High Char Yield

Resin Viscosity Suitable for Filament Winding / RTM

Good Flame, Smoke, & Toxicity Characteristics

Compatible with Thermoplastic Tougheners and Nanoscale Reinforcements

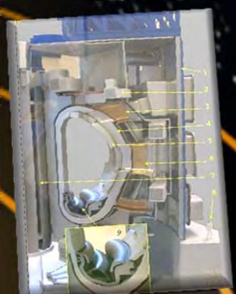
Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion



Cyanate Esters Around the Solar System

Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor



Fusion reactor, photo courtesy of Gerritse ((Wikimedia Commons)

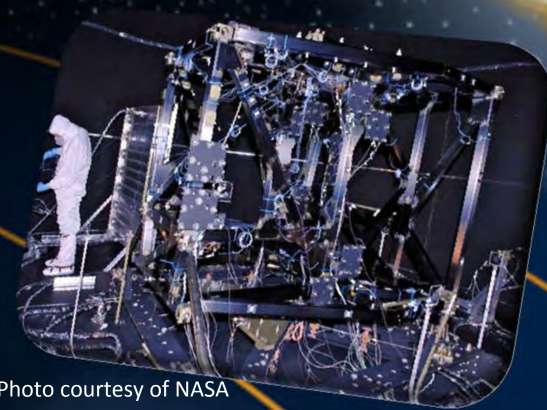


Photo courtesy of NASA

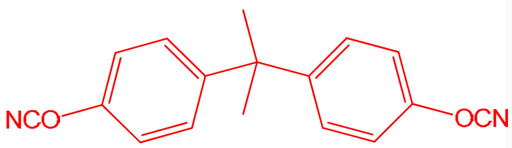
- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope

- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites

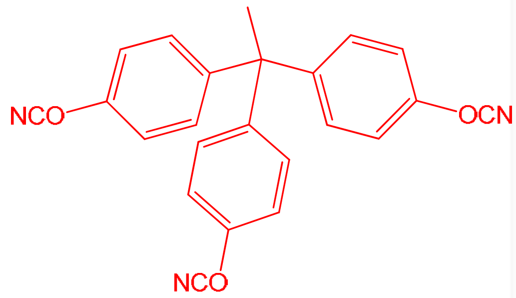
- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

Images: courtesy NASA (public release)

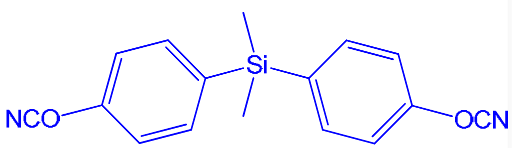
Si-Containing Cyanate Ester Monomers



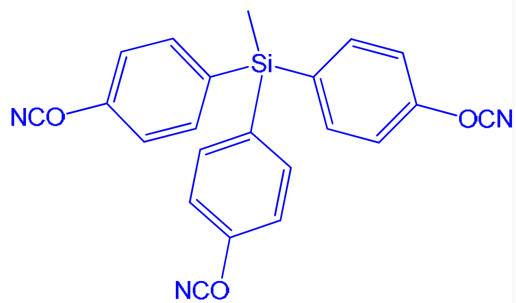
BADCy



ESR255



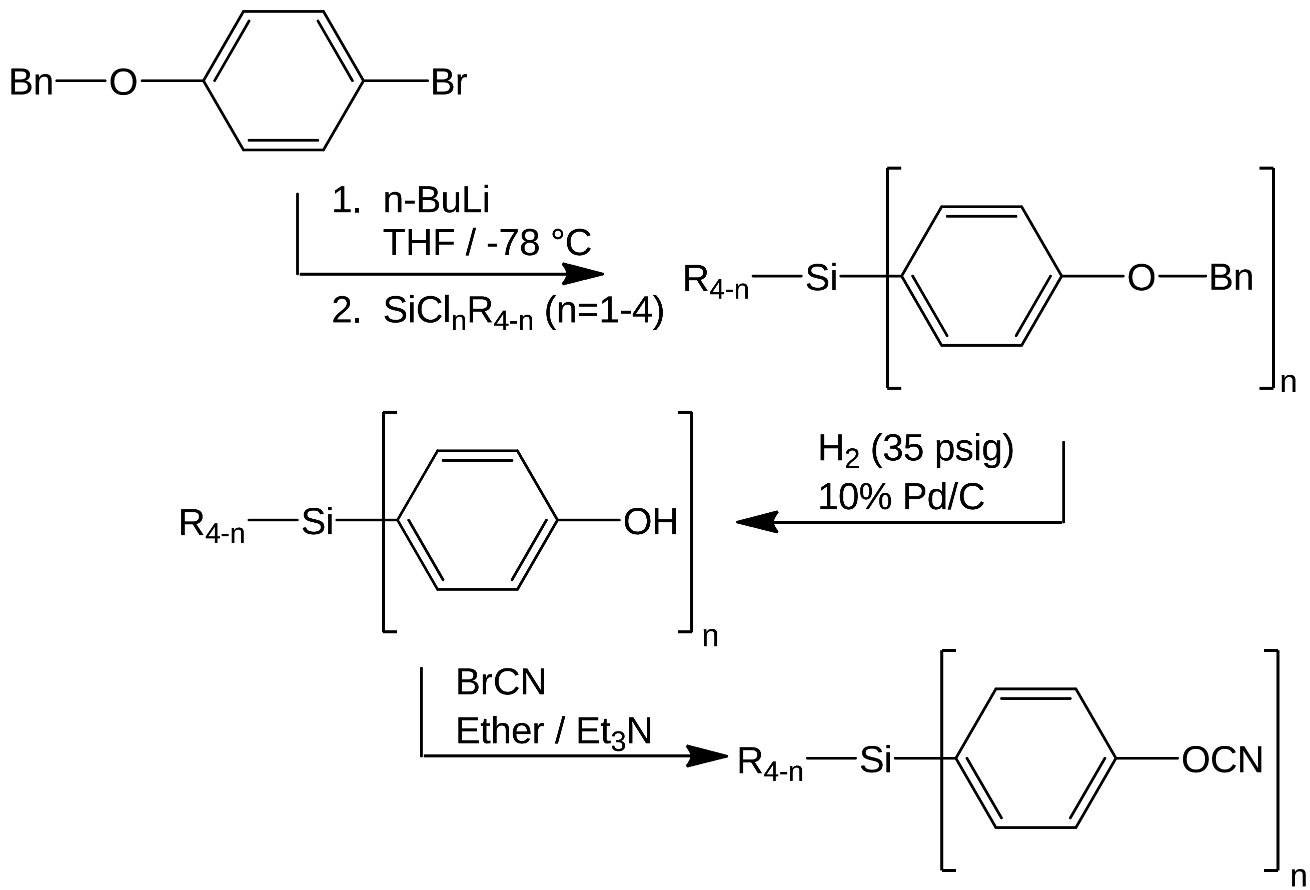
SiMCy



STT3

Catalyzed systems use:
160 ppm Cu(II) as Cu(II)(acac)$_2$ with 2 phr nonylphenol
All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N_2, cure schedule for 1 hr at 150 °C followed by 24 hrs at 210 °C, with ramp rates at 5 °C / min.

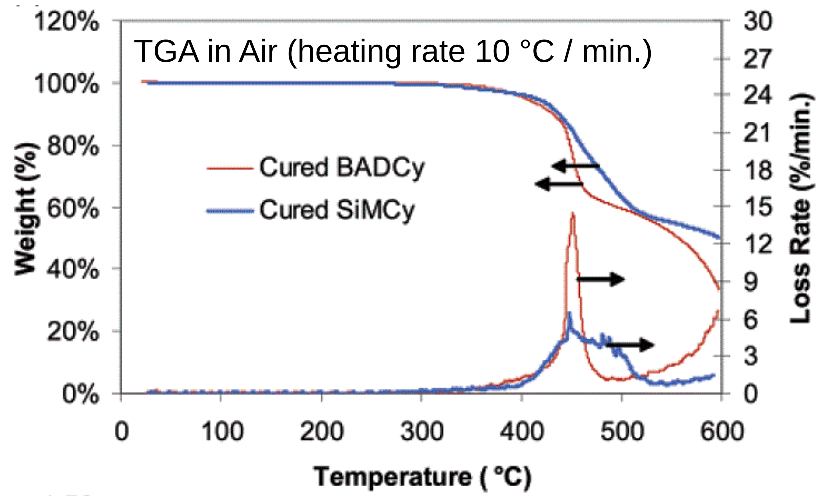
General Synthesis for Si-Containing Monomers

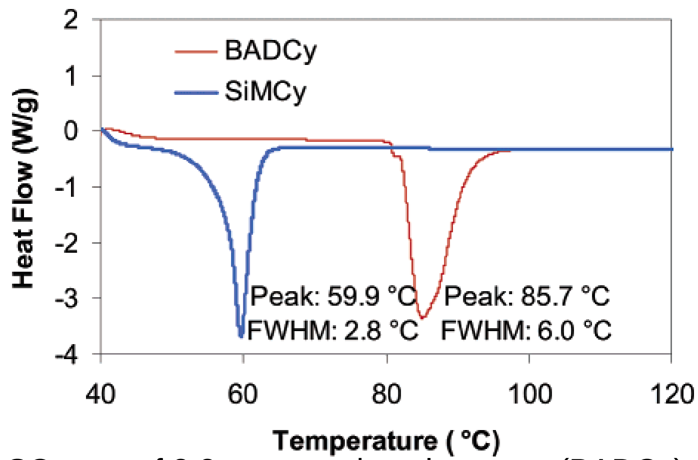


- SiMCy is the n=2 case (Si in network segment), n=3 or n=4 produces Si at network junctions

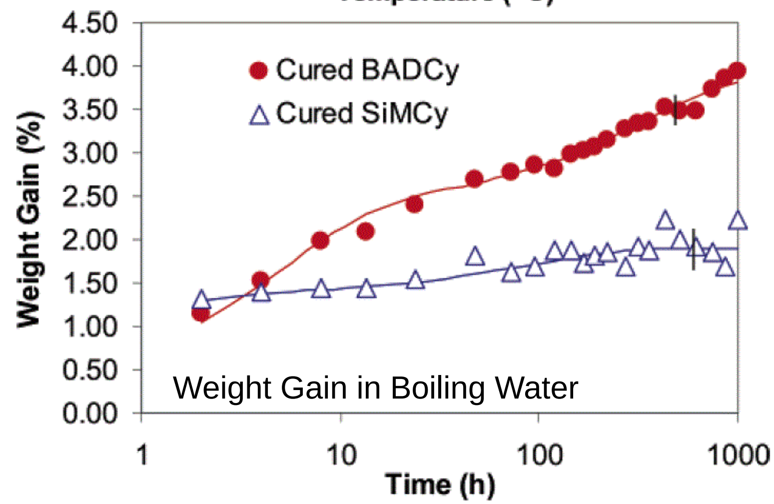
The Use of Si in Thermosetting Polymers

Silicon has mainly been used as a rigid reinforcement to promote improved mechanical and thermo-oxidative performance. Some examples of the use of silicon at a molecular level, in flexible rather than rigid form, are known (e.g. Wright et al., Polymer Preprints, 2004, 45(2), 294.



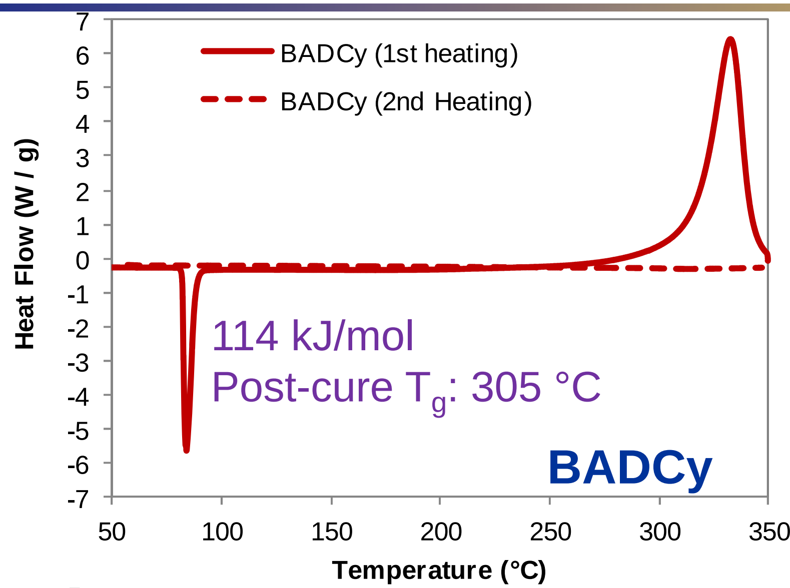


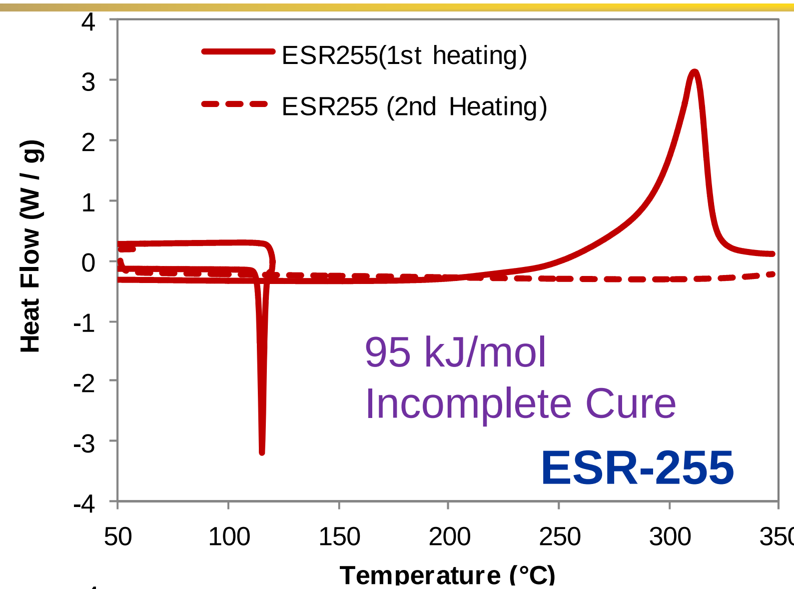
DSC scan of 2,2-cyanatophenylpropane (BADCy) and bis- (4-cyanatophenyl)dimethylsilane 3 (SiMCy) near the melting point.

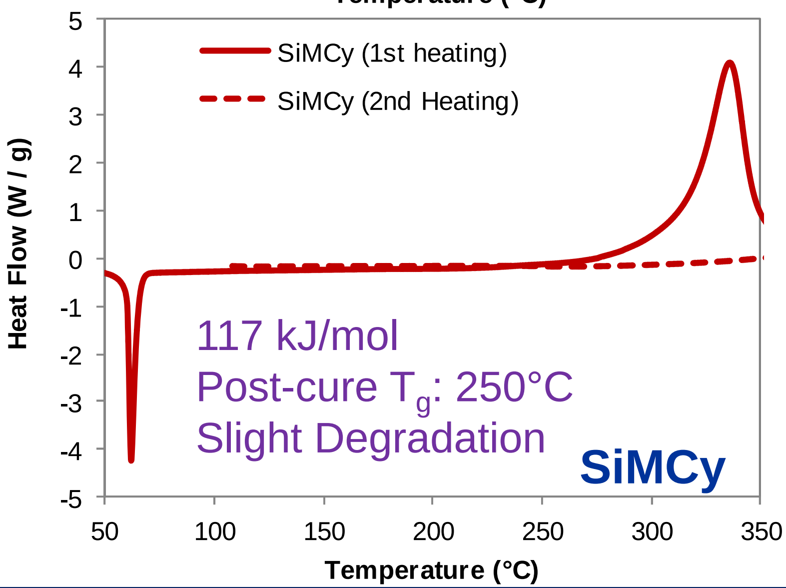


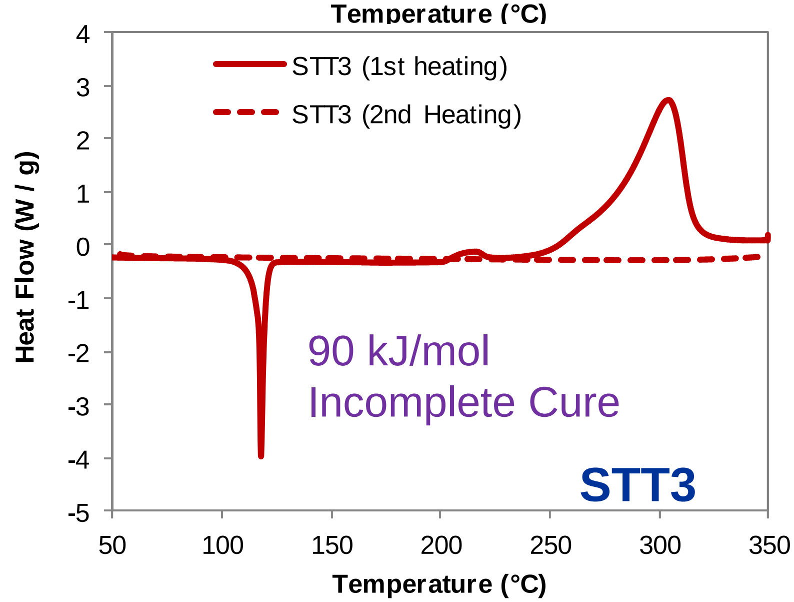
- In addition to the expected increase in short-term thermo-oxidative stability; the substitution of Si also results in lower melting temperatures and lower water uptake

Si-Containing Cyanate Esters: Non-isothermal DSC

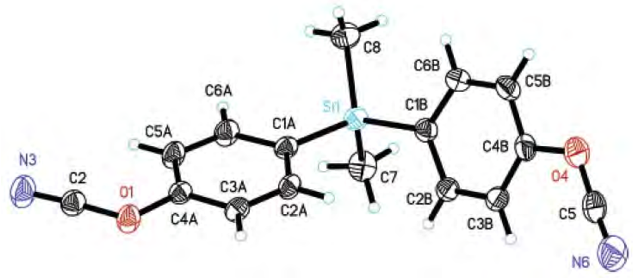


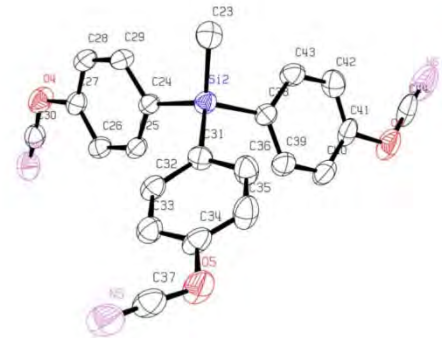






Si-Containing Cyanate Esters: Crystal / Volumetric Properties





Compound / Property	BADCy	SiMCy	ESR255	STT3
Melting Point, °C (monomer)	82.1 ± 0.2	60.4 ± 0.1	115.9 ± 0.2	117.5 ± 0.1
ΔH_m (kJ/mol, monomer)	28.4 ± 0.5	27.4 ± 0.2	29.2 ± 0.7	29.2 ± 0.3
ΔS_m (kJ/mol K, monomer)	80.0 ± 1.4	82.1 ± 0.6	75.0 ± 1.9	74.8 ± 0.8

- Incorporation of Si can improve processing characteristics by lowering the melting point of some crystalline monomers
- Enthalpies of melting vary over a surprisingly narrow range
- Entropies of melting are higher for dicyanates, with Si substitution increasing entropy of melting in dicyanates but not in tricyanates

Heuristic Models of the Effects of Silicon Substitution on Melting

- Yalkowsky model
  - Ultimately empirical, but based on simple mechanisms
  - Not designed for silicon-containing species, but general principles are easily extended to include common silicon-containing species
  - Based on underlying mechanisms, would expect no change in entropy of melting when dimethylsilylene group is substituted for isopropylidene because there is no increase in “flexibility” per the counting rules

- Chickos model
  - Empirical
  - Derived from data set on thousands of compounds
  - Predicts a higher entropy of melting for all silicon-containing compounds relative to their carbon-containing analogues
  - Magnitude of effect is +7.7 J/mol K per dimethylsilylene substitution for isopropylidene
  - No mechanism

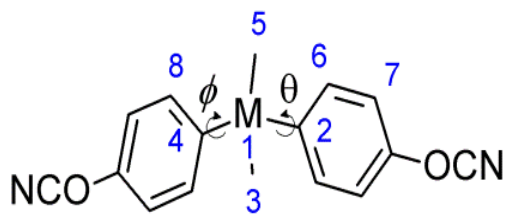
Model Predictions vs. Experiment

ΔS_m (kJ/mol K, monomer)	BADCy	SiMCy	ESR255	STT3
ΔS_m (kJ/mol K, Yalkowsky)	84	84	98	98
ΔS_m (kJ/mol K, experiment)	80.0 ± 1.4	82.1 ± 0.6	75.0 ± 1.9	74.8 ± 0.8
ΔS_m^0 (kJ/mol K, Chickos)	70	78	88	95
ΔS_m^0 (kJ/mol K, experiment)	69 ± 3	81 ± 1	50 ± 14	55 ± 3
T_m (model ΔS_m & exp. ΔH_m)				
Yalkowsky (°C)	66	54	24	24
Chickos (°C)	73	50	42	29
Experiment (°C)	82.1 ± 0.2	60.4 ± 0.1	115.9 ± 0.2	117.5 ± 0.1

- Yalkowsky model over-predicts entropy of melting for tricyanates, in part because the rules for counting anisotropy do not consider star-like arrangements, and a triphenyl substituted sp^3 is still counted as flexible. These factors explain about 70% of the error.
- Chickos model has a similar pattern of predictive success, perhaps because “bis-like” prolate organic compounds are more studied than “tris-like” “pitchfork” structures

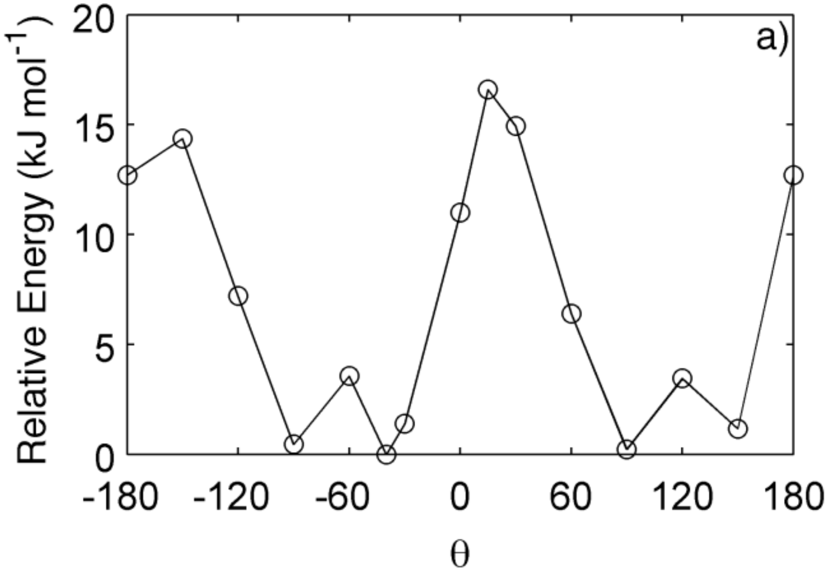
Conversion from ΔS_m^0 to ΔS_m based on $\Delta_{cp,m}$ = const. = ΔS_m; $\Delta S_m = \Delta S_m^0 / [1 - \ln (T_m / 298)]$

Molecular Modeling Studies of CE Monomers

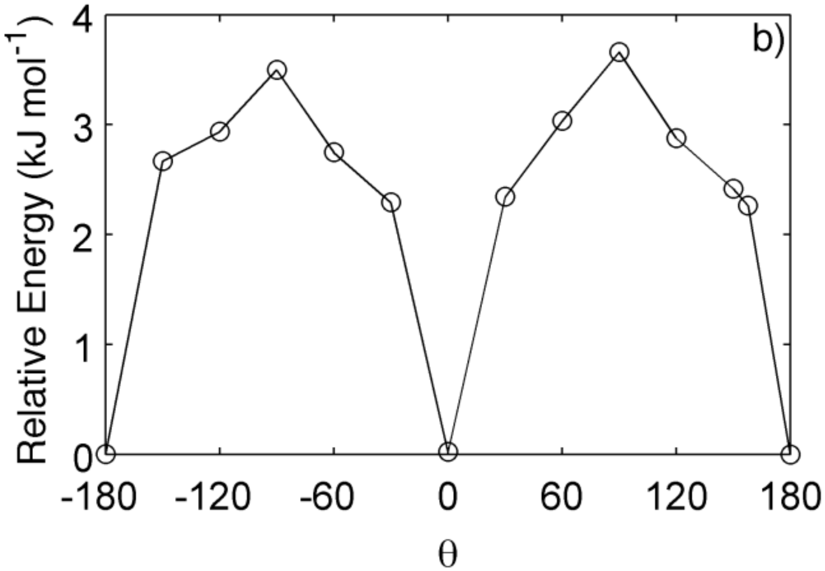


PM3 semi-empirical method chosen due to high relative accuracy in Si-C bond lengths

BADCy (M = C)

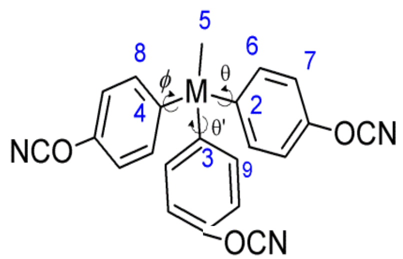


SiMCy (M = Si)



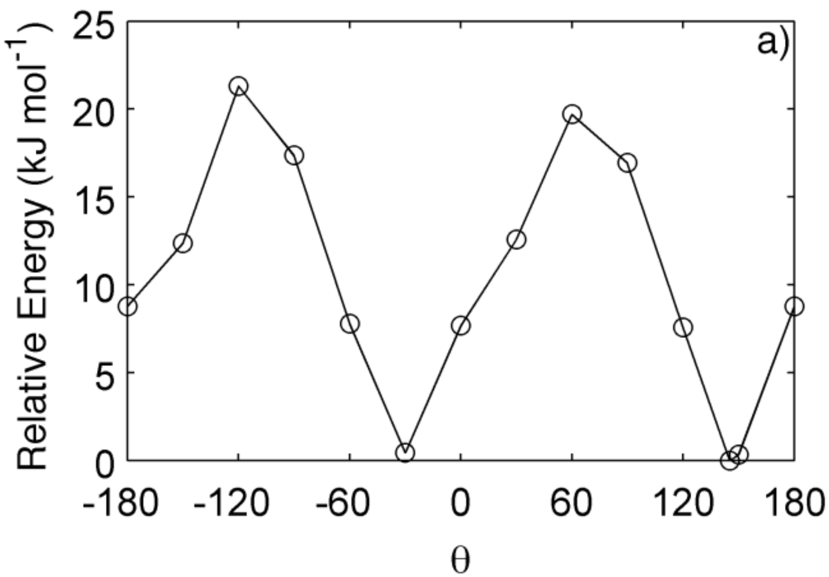
- Relative dihedral rotation of phenyl rings is strongly hindered in BADCy but not in SiMCy in the isolated molecule
- SiMCy should therefore have more available conformations in the melt, leading to a higher entropy of melting

Molecular Modeling Studies of CE Monomers

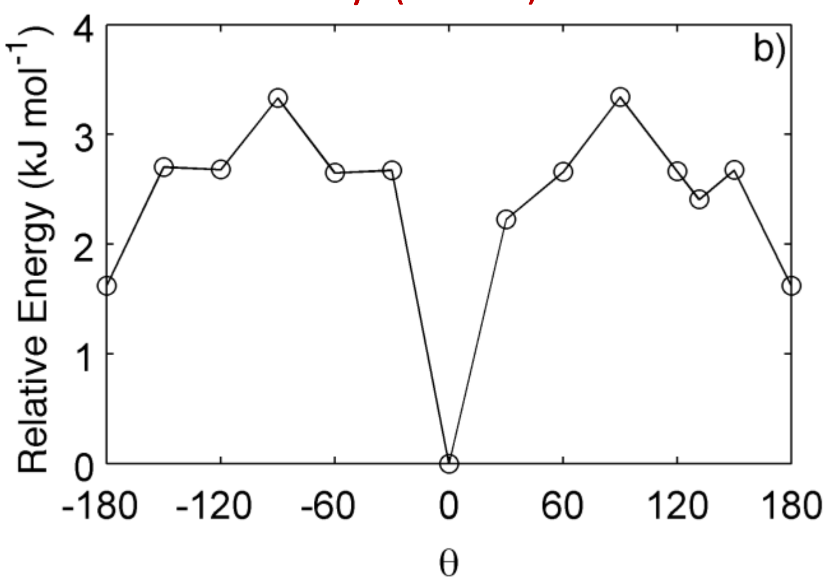


Only ϕ fixed

BADCy (M = C)

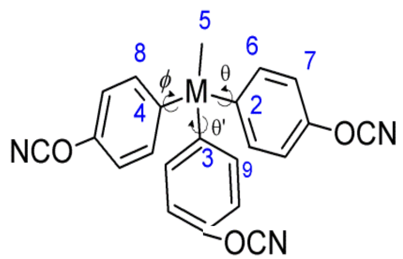


SiMCy (M = Si)



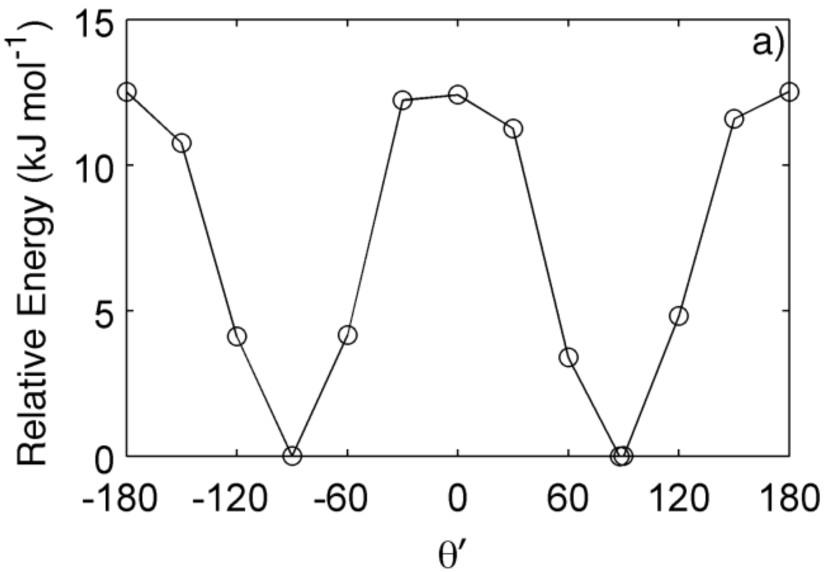
- In the tricyanate monomers also, the longer C-Si bond permits greater relative torsional rotation of phenyl rings

Molecular Modeling Studies of CE Monomers

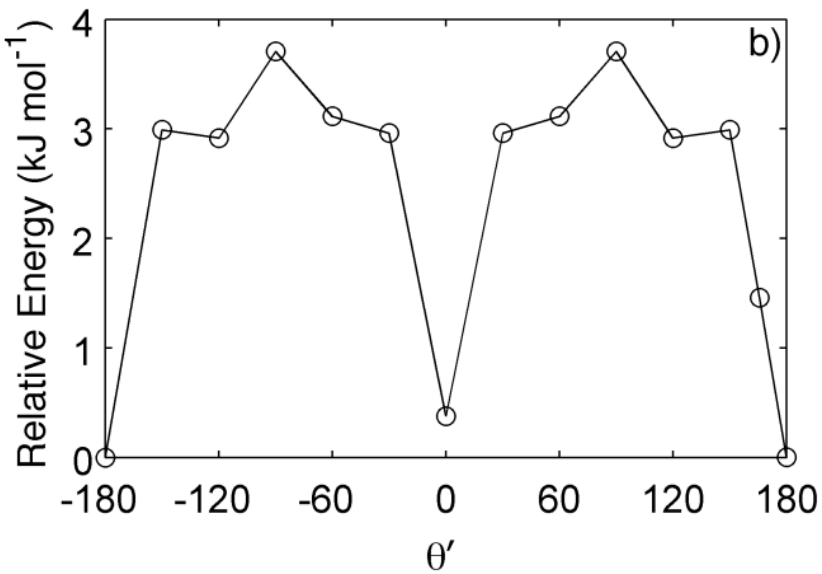


θ and ϕ fixed at 180 °

ESR-255 (M = C)



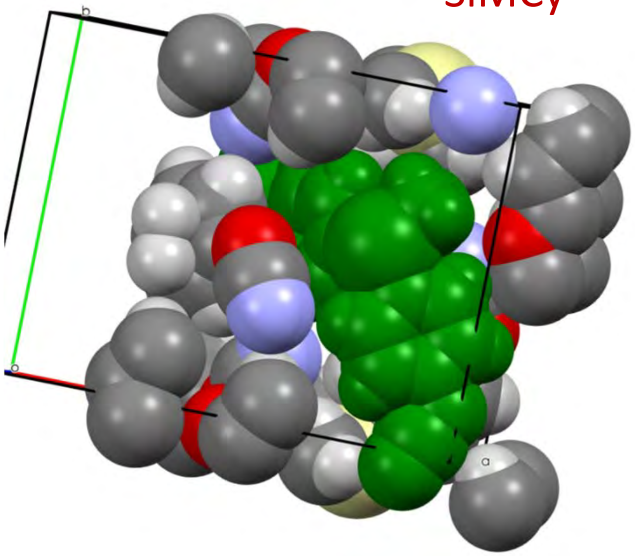
SiCy-3(M = Si)



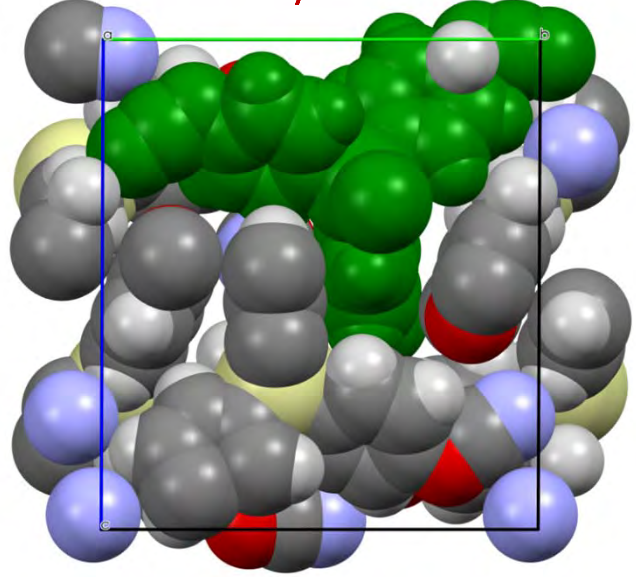
- In SICy-3, when two of the phenyl groups are in the correct configuration, the third phenyl group is free to rotate

Effect of Molecular Shape

SiMCy



SiCy-3



- Dicyanates tend to maintain a relatively simple prolate shape, whereas tricyanates have a star-like shape that allows for a greater degree of “intermeshing” with neighboring molecules.
- In the liquid state, intermolecular constraints may be more important in constraining the motion of tricyanates, meaning intramolecular effects (such as free relative rotation of phenyl rings) are suppressed.
- A similar effect may explain the differences in the enthalpy of melting.

Summary

- Incorporation of silicon into organic molecules can have interesting secondary effects beyond simply making some bonds longer and more flexible.
- In cyanate esters, incorporation of silicon into dicyanates lowers the melting point by 22 °C, providing a significant boost to ease of processing for operations such as filament winding. In symmetric tricyanate esters, however incorporation of silicon does not have the same beneficial effect.
- Investigations using both heuristic and semi-empirical molecular models appear to show that these differences in behavior arise because of the relative importance of intra- and inter-molecular constraints on motion in the liquid state.
- The key to taking advantage of longer C-Si bonds to lower the melting point of multi-functional monomers appears to be maintaining a compact, prolate, rather than star-like, molecular shape.

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